Design Principles for the Use of Electroactive Polymers for Overcharge Protection of Lithium-Ion Batteries

Karen E. Thomas-Alyea, John Newman, Guoying Chen, and Thomas J. Richardson

Department of Chemical Engineering, U.C. Berkeley, and Energy and Environmental Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720.

Abstract

A continuum-scale model is presented to explain how electroactive polymers such as polythiophene can be used to provide overcharge protection for lithium-ion batteries. The model shows how the cell is transformed upon overcharge from a battery to a resistor with a resistivity that varies with position across the separator. Upon discharge or open circuit, self discharge transforms the resistor back into a battery, and normal cycling can be resumed. A simplified model yields a design equation that shows how the potential at which the cell shorts depends on the current density, separator thickness, and the variation of the electronic conductivity and the oxidation potential of the polymer with degree of oxidation. The shorting voltage is independent of the choice of positive electrode and scales with the potential of the charged negative electrode.

Introduction

Batteries using nonaqueous electrolytes, such as lithium-ion batteries, are attractive for applications requiring high energy density, because the nonaqueous electrolyte enables high cell voltages. However, overcharge of a cell containing a nonaqueous electrolyte can cause irreversible, exothermic degradation, leading to the risk of thermal runaway and explosion. This risk is exacerbated in a large battery comprised of many cells in series. In a string of cells connected in series, the same amount of current passes through each cell. If the capacity of one cell in the string is lower than the others, either because of imprecision in manufacturing or uneven rates of degradation, then the weaker cell will be overcharged and overdischarged if the full capacity of the stronger cells is utilized. The abuse of the weaker cell will cause its capacity to fade even more rapidly, exacerbating its defects and leading to risk of catastrophic failure.

There are many requirements for an overcharge protection device for a large series-connected string of cells. The device must prevent the cell's potential from exceeding a certain voltage. However, the device should maintain the cell's potential at the cutoff voltage in order to allow complete charging of the other cells in the string before the cutoff potential for the string is reached, but without overcharging the other cells. The device should not interfere with the cell chemistry or with thermal management of the cell. It should have small mass, volume, and cost. It should not cause a large leakage current. Finally, the device should be reversible, in that the cell should return to normal performance after cessation of overcharge.

Two previous patents[1, 2] have suggested the use of electroactive polymers for overcharge protection. There are many examples of electroactive polymers, such as polyacetylene, polythiophene, and polypyrrole. They have the distinguishing characteristic of changing from electronic insulators to metallic conductors upon oxidation. The oxidation of the polymer is accompanied by insertion of an anion into the polymer. The idea for using the electroactive polymers for overcharge protection is as follows. During normal cell operation, the potential of the positive electrode lies below the oxidation potential of the electroactive polymer, and the polymer stays in its insulating state. If the cell is overcharged, its potential rises above the oxidation potential of the polymer, causing oxidation of the polymer, leading to growth of an electronic short across the cell.

In a previous publication [3], we have proven that the idea is feasible using a commercially available electroactive polymer, and have demonstrated that cells can be protected against overcharge by incorporation of electroactive polymers into the separator of the cell. In this paper, we use computer simulations to elucidate the processes occurring in the cell during the formation of the electronic short and present a design equation for the effect of key parameters on the voltage at which the cell shorts.

Full model

The model cell configuration is as follows. The positive electrode is comprised of an intercalation material whose potential varies with state of charge, such as $LiTiS_2$. The separator consists of a porous, inert, mechanical separator whose pores are partially filled with the electroactive polymer, the remaining void space being filled with elec-

trolyte. We use poly(3-butyl thiophene) as the electroactive polymer, and $LiPF_6$ in 1:1 ethylene carbonate : dimethyl carbonate as the electrolyte. For brevity, we shall refer to the electroactive polymer as PBT. Experimentally, one could add the PBT to the separator by dipping the separator in a solution of dissolved, chemically synthesized PBT, and then evaporating the solvent to leave a separator-PBT composite membrane.[3] For simplicity, the negative electrode is lithium metal.

The electroactive polymer initially is in its insulating state. If exposed to a potential positive of its oxidation potential, the polymer can be oxidized. When oxidized, an anion A from the electrolyte is inserted to balance the charge according to the reaction

$$n\mathrm{T} + ny\mathrm{A}^- \rightarrow n\mathrm{A}_y\mathrm{T} + nye^-, \tag{1}$$

where T represents a monomer unit of the polymer. We refer to the number of anions inserted per unit monomer as y, which is the degree of oxidation of the polymer. For most electroactive polymers, y has a range between 0 and about 0.3. The electronic conductivity σ of the polymer increases by nearly 8 orders of magnitude with increasing degree of oxidation. In addition, the thermodynamic potential, U, also called the open-circuit potential or the oxidation potential, varies with degree of oxidation.[4]

In regular battery models,[5, 6] the potential in the electronically conducting phases Φ_1 is discontinuous across the cell, being governed by Ohm's law in each electrode but having no meaning in the electronically insulating separator. In contrast, in the present model, Φ_1 is considered to be continuous across the entire cell, while σ differs in the three regions of the cell (positive electrode, negative electrode, and separator) and varies with degree of oxidation of the polymer. Nowhere does the model specify the amount of ionic current in the electrolyte, in contrast to normal battery models. Solving the coupled equations yields the amount of current that goes into solution versus the amount of current that flows as an electronic short, according to the balance among the electronic ohmic resistance of the separator and the kinetic and ionic ohmic resistances of the electrodes and electrolyte. A detailed description of the equations and assumptions used in the model can be found in reference [7].

Figure 1 shows a simulated galvanostatic overcharge at 1 mA/cm^2 of a $LiTiS_2$ | Li cell with and without overcharge protection. The potential of the unprotected cell increases rapidly as the $LiTiS_2$ nears full charge. Experimentally, the cell potential would not rise indefinitely, but would level off as unwanted side reactions occurred at the higher potentials. In contrast to the unprotected cell, the simulated potential of the cell containing the electroactive polymer levels off to a constant value as the cell is overcharged. We refer to the value of this cell potential as V_{ss}. One can pass current indefinitely without further change in the cell potential. The simulated behavior matches that observed experimentally[3] and indicates that the polymer is able to form an electronic short across the cell.

Interestingly, the polymer "short" occurs at 4 V. This result makes the polymer short an ideal overcharge-protection mechanism to protect a cell in a large stack, because the potential of the overcharged cell would remain constant at V_{ss}, allowing other cells in a series-connected string to reach full charge without in turn being overcharged. However, one ordinarily expects that a cell's potential would drop to near zero if the cell were electronically shorted. How, then, can there be an electronic short while maintaining such a high cell potential?

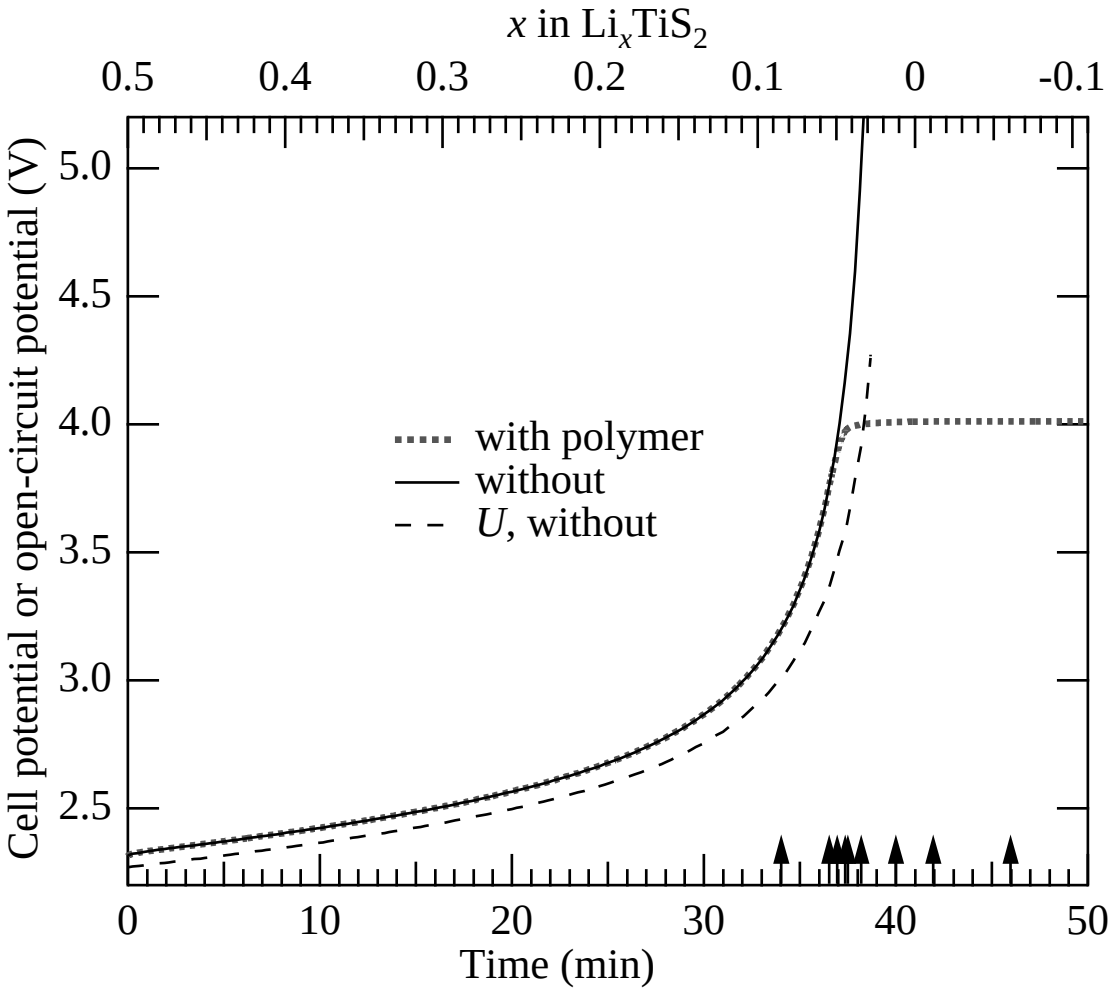

Figure 1: Simulated overcharge at 1 mA/cm^2 of a Li | TiS_2 cell with and without electroactive polymer present for overcharge protection. Also shown is the open-circuit potential of the Li_xTiS_2 (dashed line) as a function of time and state of charge. Arrows indicate the times at which profiles are drawn in Figures 2.

To answer this question, we examine the simulated profiles of degree of oxidation across the separator, shown in Figure 2. The profiles are shown for different times during the charge given in Figure 1. During normal cell operation, when the unprotected and protected cells exhibit identical behavior, the polymer is entirely in its neutral state ($y = 0$). When the potential at the positive electrode exceeds the oxidation potential of the polymer, the polymer begins to be oxidized. Because the unoxidized polymer is so resistive, the oxidation reaction moves as a front across the separator rather than being uniformly distributed across the polymer.

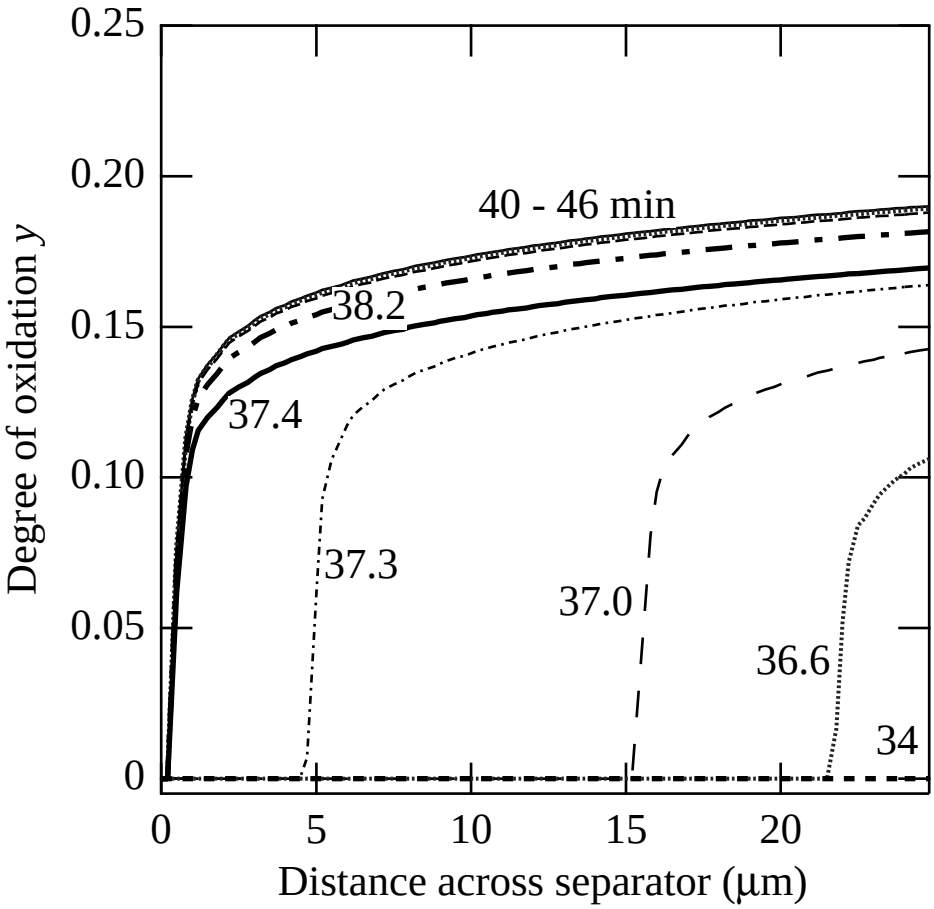

Figure 2: Degree of oxidation of the polythiophene as a function of position across the separator. Time in minutes, corresponding to the time during charge as shown in Figure 1, is indicated as a parameter. The profiles at 40, 42, and 46 minutes are nearly indistinguishable.

At 37.4 minutes, the amount of current going into solution at the negative electrode is less than the total current being galvanostatically applied to the cell. The difference is the electronic current $\mathbf{i}_1$ passing through the electroactive polymer. The percent of the total current which is electronic rises to nearly 100% by 46 minutes. At this point, the cell can be termed a "resistor" instead of a "battery," as the current in the separator is electronic, not ionic. The complete change from "battery" to "resistor" is a gradual transition that takes nearly 10 minutes, during which some of the current in the separator is carried electronically while the remainder is ionic. It

takes less than 2 minutes for half of the current to switch from ionic to electronic.

After 46 minutes, the state of the cell ceases to change with time, and it can be termed to have reached a "steady state." There are two interesting features of the profile for the degree of oxidation at steady state. First, the oxidation front never extends entirely across the cell. The polymer remains in its neutral state adjacent to the negative electrode, and there is a smooth increase in degree of oxidation across the separator. Second, the maximum degree of oxidation, which occurs adjacent to the positive electrode, is equal to 0.19. This is less than the maximum possible degree of oxidation of poly(3-butylthiophene), which is about 0.28. Thus, the polymer does not necessarily become fully oxidized when a short forms.

The profile of $y(x)$ across the cell determines the profile of the potential drop between the potentials of the positive and negative electrodes. Initially, the potential drop occurs linearly across the separator, which carries miniscule electronic current during normal cell operation, according to Ohm's law and the very low conductivity of the neutral polymer. As the polymer becomes oxidized, its conductivity increases. The potential drop therefore must be sustained by an insulating region somewhere in the polymer. This insulating region is found near $x = 0$ because the reducing potential of the negative electrode keeps the polymer in its neutral state there. At "steady state" overcharge, the polymer thus functions as a resistor between two voltage sources, with a state of oxidation and thus resistivity which varies with position across the separator. Most of the potential drop occurs across a very narrow region next to the negative electrode.

Simplified model

The simulations shown above provide insights that allow one to develop a simplified model of the system during steady-state overcharge. At steady state, electrochemical reaction and mass transport in the electrolyte are negligible, and the system behaves essentially as a resistor. A resistor is described simply by Ohm's law,

$$\mathbf{i}_1 = -\sigma \nabla \Phi_1. \tag{2}$$

Since all of the current is electronic, $\mathbf{i}_1$ is equal to I, the total applied current. If no reaction is occurring, then there can be no driving force for reaction; that is, there can be no surface overpotential. Therefore, at every point in space, the potential in the conducting polymer, Φ_1, must be equal to the thermodynamic potential, U, which depends on the degree of oxidation y. Thus, equation 2 can be rewritten as

$$I = -\sigma\left(y(x)\right)\frac{dU\left(y(x)\right)}{dx} = -\sigma(y)\frac{dU(y)}{dy}\frac{dy}{dx}, \tag{3}$$

where for simplicity we have treated the cell as one-dimensional.

The boundary condition for this equation depends on the state of the polymer adjacent to the negative electrode. Let $x = 0$ at the negative electrode-separator interface and let $x = L_s$ at the positive electrode-separator interface. Because Φ_1 is continuous across the cell, the potential of the polymer immediately adjacent to the negative electrode is fixed by the potential of the negative electrode. Because there can be no surface overpotential, the potential in the polymer fixes its degree of

oxidation at that position. Polythiophene is in its neutral state for potentials lower than 2 V, which is higher than the potential of negative electrodes of interest for lithium batteries. Therefore, we can use

$$y = 0 \text{ at } x = 0 \tag{4}$$

as the boundary condition.

Integrating equation 3 then yields an implicit equation for y as a function of x,

$$x = -\frac{1}{I}\int_0^y \sigma \frac{dU}{dy'} dy'. \tag{5}$$

Equation 5 represents a simplified model for the behavior of the system during steady-state overcharge. One sees from this equation that the parameters governing the behavior of the short are the current density I, the separator thickness L_s, the conductivity σ as a function of y, and the slope of the oxidation potential of the polymer U with degree of oxidation.

The potential of the cell is the potential at the positive current collector minus the potential at the negative current collector:

$$V_{ss} = U\left(y(x = L_s)\right) - \Phi_1(\text{negative electrode}). \tag{6}$$

We see that the potential of the cell, V_{ss}, is *completely independent* of the nature of the positive electrode. In other words, the potential at which a short will form depends only on the nature of the electroactive polymer in the separator. Barring any chemical interaction of the electroactive polymer with the positive electrode, a given electroactive polymer can be used to provide overcharge protection for any cell chemistry (within the limits of the electroactive polymer as specified below).

Integrating equation 5 across the separator yields

$$L_s \leq -\frac{1}{I}\int_0^{y_{\max}} \sigma \frac{dU}{dy'} dy'. \tag{7}$$

This equation tells us the two limits of the ability of a given electroactive polymer to short a cell. The first limitation is that the short may occur at such a high value of V_{ss} that the PBT is damaged irreversibly, impairing its performance on subsequent overcharge events. Most electroactive polymers become oxidized irreversibly above some threshhold $y_{\max}$, equal to about 0.3 for most polythiophenes. Thus, $y(x = L_s)$ must be less than y_{max} to avoid degradation of the electroactive polymer. Therefore, V_{ss} should not be higher than $U(y_{max})$. As a consequence, a given electroactive polymer can protect a cell only within a potential range that is lower than its degradation potential. This may prove to be a serious limitation of the use of electroactive polymers to protect high-potential positive electrodes against overcharge. The poly(3-butyl thiophene) used in this investigation is stable up to about 4.2 V. Research is needed to find polymers with other substituents which may have a higher oxidative stability window.

The second limitation determines whether or not a short forms at all. If $\sigma(y)$ is too low, or L_s or I is too high, then there may be no solution to equation 7. An electroactive polymer with a higher conductivity or a thinner separator would be required to enable shorting of the cell.

The simple model presented above shows that the parameters governing the steady-state behavior of the short are L_s, I, $\sigma(y)$, and $\partial U/\partial y$. The simple model also allows one to identify how these parameters affect its behavior. There are several factors to consider when describing the behavior of the short. The most important factor is V_{ss}, as the purpose of the short is to allow the cell to reach full charge without being overcharged. V_{ss} depends on $y(L_s)$ and $U(y)$ as given by equation 6. A second factor is the amount of charge required to form the short, which will determine how quickly the short forms and how much the negative electrode must be oversized. The amount of charge required is determined by the profile of $y(x)$. A third consideration is how much self-discharge will occur after the charging current is turned off. At the end of overcharge, the electroactive polymer in the separator is electronically conducting. When the current is turned off or reversed, electronic current will still be able to flow through the internal short, causing both reduction of the polymer back to its insulating state and self discharge of the positive electrode. The effect of L_s, I, and σ on these three factors is given in Table 1. The fourth governing parameter, $\partial U/\partial y$, determines the degree to which the other three parameters affect V_{ss}. The smaller $\partial U/\partial y$, the less V_{ss} will change with a change in L_s, I, or σ.

Table 1: Qualitative effects of increasing current density, separator thickness, and electronic conductivity on the profile of the degree of oxidation of the polymer, the shorting voltage, and the amount of self-discharge.

	$y(x)$	V_{ss}	self-discharge
$\uparrow I$	$\uparrow$	$\uparrow$	$\uparrow$
$\uparrow L_s$	-*	$\uparrow$	$\downarrow$
$\uparrow \sigma(y)$	$\downarrow$	$\downarrow$	$\uparrow$

*Increasing the separator thickness does not change the slope of the $y(x)$ profile, although increasing L_s does increase the value of $y(L_s)$.

The effect of L_s and I is illustrated in Figure 3, which shows steady-state profiles for y for different values of the current density. As described in equation 6, the value of y at the positive electrode-separator interface is what determines the shorting voltage. Figure 4 shows how the shorting voltage V_{ss} depends on I for a separator thickness of 25 μm.

Conclusions

The use of an electroactive polymer incorporated into a battery's separator is an attractive new option for overcharge protection. It meets most of the criteria for an overcharge-protection device for large batteries, in that it is cheap, light-weight, compact, reversible, prevents the cell from exceeding the cutoff voltage, and holds the potential at the cutoff voltage indefinitely. Further study is needed to verify the long-term durability of the electroactive polymer in the environment of the lithium-ion battery.

The model, in both its complete and simplified forms, has shown qualitative agreement with all experiments performed to date.[4] The behavior of the short is governed

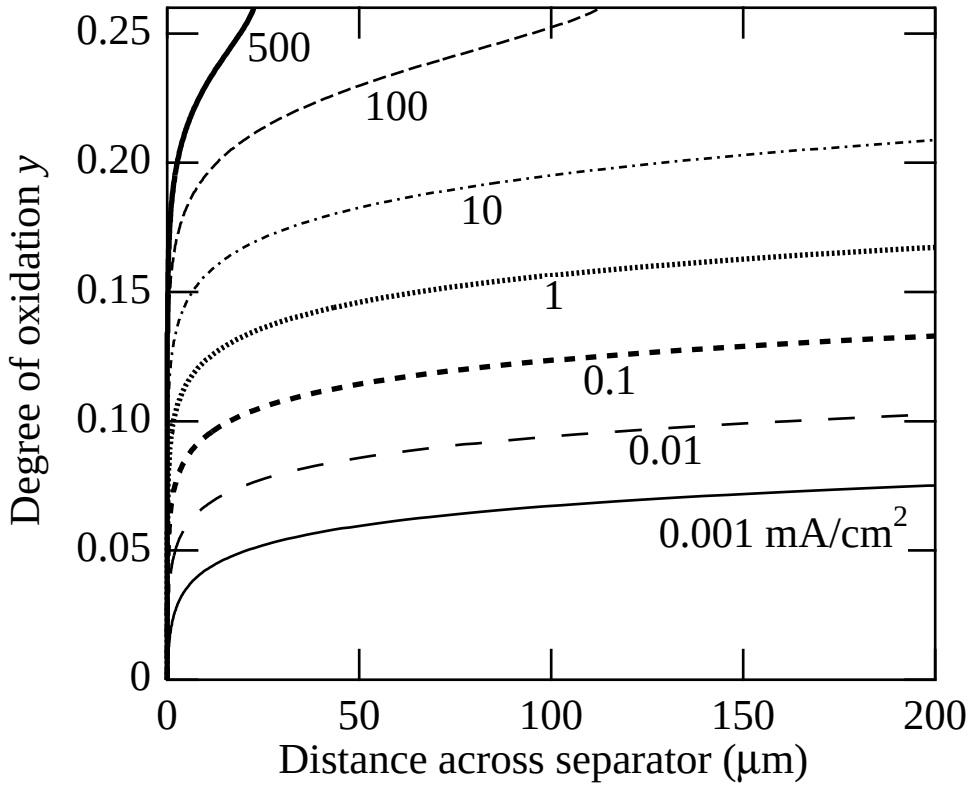

Figure 3: Steady-state profiles of the degree of oxidation as a function of distance from the negative electrode, for different values of the current density indicated as a parameter.

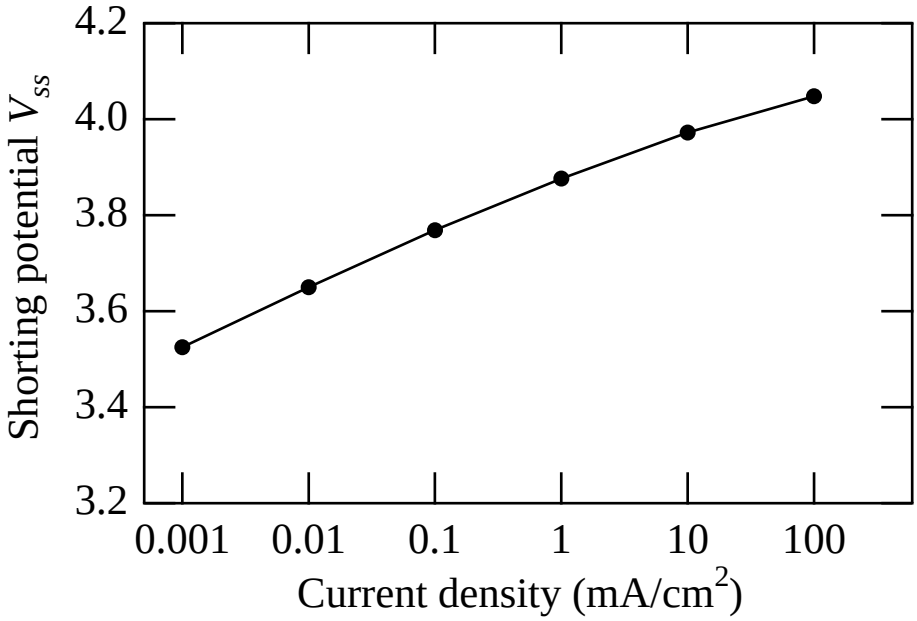

Figure 4: Shorting voltage as a function of current density for a 25 μm-thick separator. V_{ss} changes only slightly with current density because $U(y)$ for the polythiophene is relatively flat.

by the profile of the degree of oxidation across the separator. The polymer is in the completely neutral state adjacent to the negative electrode, and is more oxidized (but not necessarily fully oxidized) adjacent to the positive electrode. The submicrometer-thick insulating region next to the negative electrode is what allows the cell to be electronically shorted but still maintain a high cell potential, which is a desirable feature for an overcharge-protection device. The steady-state behavior of the short and thus the shorting potential V_{ss} are functions of I, L_s, σ, and $\partial U/\partial y$. Table 1 summarizes the effect of these parameters on the steady-state behavior of the short. The principles summarized in this table can be used to select an electroactive polymer with a particular $U(y)$ and then tailor its morphology to create a conductivity in the separator that forms a short with a desired dependence of V_{ss} on the applied current density. To minimize the self discharge, one would want to have the most resistive morphology of the electroactive polymer that still provides a short at the desired shorting voltage. V_{ss} is independent of the nature of the positive electrode and scales with the potential of the charged negative electrode.

The limitations of the electroactive polymer are expressed in equation 7. V_{ss} must be less than $U(y_{max})$ or else irreversible degradation of the short will occur. $\sigma(y)$ must be high enough that equation 7 can be satisfied or else a short will not form.

References

[1] F. Denton, J. N. Howard, A. A. Anani, and J. M. Fernandez. U.S. Patent 6,228,516, 2001.

[2] H. Mao and D. S. Wainwright. U.S. Patent 6,074,766, 1990.

[3] G. Chen, T. J. Richardson, K. E. Thomas, and J. Newman, *Electrochem. and Solid State Letters*, ((submitted 2003)).

[4] G. Chen, T. J. Richardson, K. E. Thomas-Alyea, and J. Newman. in progress, 2003.

[5] T. F. Fuller, M. Doyle, and J. Newman, *J. Electrochem. Soc.*, **141**, 1 (1994).

[6] K. E. Thomas, R. M. Darling, and J. Newman, *Advances in Lithium-Ion Batteries*, ch. Modeling of Lithium Batteries. Kluwer Academic Publishers, New York, 2002.

[7] K. E. Thomas-Alyea, J. Newman, G. Chen, and T. J. Richardson *J. Electrochem. Soc.*, (submitted 2003).

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